

Thienothiophenes. Part 3.^{1,2} On the ring-opening reactions of 3-lithiated and 3,6-dilithiated thieno[3,2-*b*]thiophenes; new routes to polyfunctionalized thiophenes and enediynes

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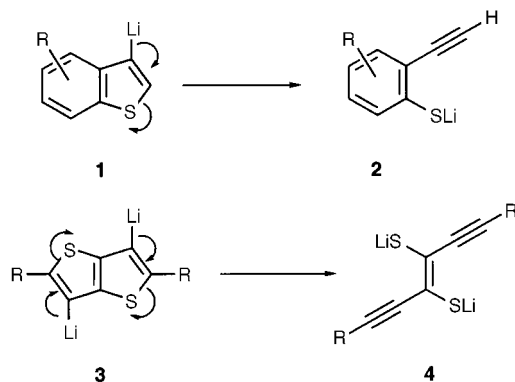
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Solutions of 2,5-disubstituted 6-bromothieno[3,2-*b*]thiophen-3-yl lithium and 3,6-dilithiothieno[3,2-*b*]thiophene in tetrahydrofuran were prepared at $-78\text{ }^{\circ}\text{C}$ from variously 2,5-disubstituted 3,6-dibromothieno[3,2-*b*]thiophenes *via* Br \rightarrow Li exchange with one or two mol equiv. of butyllithium, respectively, and allowed to warm up, when they gave derivatives of 3-bromo-5-ethynylthiophene-4-thiol and 3,4-dimercaptohex-3-ene-1,5-diyne by ring-opening processes (novel tandem ring-opening in the case of the dilithiated starting material). The products can be manipulated further before isolation.

In the mid to late 1960s we discovered that ethereal (Et₂O or THF) solutions of benzo[*b*]thiophen-3-yl lithium³⁻⁵ and its derivatives⁴⁻⁶ (prepared from a 3-bromobenzo[*b*]thiophene *via* Br \rightarrow Li exchange with BuLi at $-78\text{ }^{\circ}\text{C}$) undergo a ring-opening process, 1 \rightarrow 2, as the solutions are warmed up, to give the lithium salt of an *o*-mercaptophenylacetylene as the initial product (Scheme 1). These can react further, *e.g.* by *S*-butylation with



Scheme 1

the bromobutane produced by the initial Br \rightarrow Li exchange reaction or through metallation of the terminal alkyne. Following a report in 1962^{7,8} that “unsaturated aliphatic products” may arise when handling 3-thienyllithium, Gronowitz and Frejd⁹ reported in the late 1960s that a similar ring-opening process occurs with thiophen-3-yl lithium, to give an enyne. These early discoveries were followed by an exhaustive examination by Gronowitz’s group of the ring-opening reactions of 3-thienyllithium and a variety of its derivatives^{4,9-14} (including 1,1-dioxides^{12,14}).

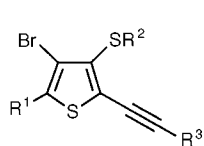
At the time of our earlier work we had considered investigating the tandem ring-opening reactions of β,β' -dilithiated thienothiophenes, *e.g.* 3 \rightarrow 4, but because the starting materials were not readily accessible¹ and our interest in other work diverted our attention, the idea was not pursued. Prompted by intense current interest in enediynes as precursors to more

complex molecular architectures¹⁵ we can now report that these reactions are feasible. We believe that the tandem ring-opening process, 3 \rightarrow 4, is the first recorded example of its kind. We have also shown that manipulation of the products 4 is also possible, *e.g.* by *S*-alkylation either with the bromobutane generated *in situ* or by an added alkylating reagent (in these cases it is preferable to carry out the initial Br \rightarrow Li exchange reaction with MeLi or PhLi) or by removal of a silyl protecting group (R) from the alkyne moieties. Our starting material is 2,3,5,6-tetrabromothieno[3,2-*b*]thiophene, the availability of which we¹ have improved recently. Its 2- and 5-bromine atoms can be replaced by other functionality either by Br \rightarrow Li exchange strategies¹ or by Pd(0)-catalyzed coupling techniques, as now reported briefly. The 3- and 6-bromine atoms remaining allow us to prepare the β -lithiated derivatives which are required for ring-opening, *e.g.* 3 \rightarrow 4. Essentially, the thieno[3,2-*b*]thiophene ring, an enediyne equivalent, is a template to which we can attach a variety of functional groups prior to effecting the ring-opening process, 3 \rightarrow 4.

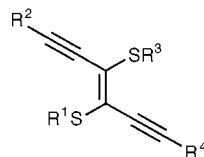
First we established that ring-opening is possible in a step-wise fashion. Thus 2,3,5,6-tetrabromothieno[3,2-*b*]thiophene was treated successively with 2 mol equiv. each of butyllithium (THF, ambient temperature) and *tert*-butyldimethylsilyl chloride, then the resulting solution of 3,6-dibromo-2,5-bis(*tert*-butyldimethylsilyl)thieno[3,2-*b*]thiophene (see ref. 1) was cooled to $-78\text{ }^{\circ}\text{C}$ when 1 mol equiv. of butyllithium was added. The resulting mixture was allowed to warm up to ambient temperature, then it was quenched by addition of aqueous ammonium chloride and the product was extracted with ether and flash chromatographed on silica. Light petroleum eluted 3-bromo-2-*tert*-butyldimethylsilyl-5-*tert*-butyldimethylsilyl-ethynyl-4-butylsulfanylthiophene 5 (70% yield) (in this case the thiolate anion captures the bromobutane generated *in situ*) as a yellow oil. Likewise 3,6-dibromo-2,5-dimethylthieno[3,2-*b*]thiophene afforded the tetrasubstituted thiophene 6 (38%) as a colourless oil (flash chromatographed on neutral alumina; light petroleum as eluant). From an attempt to synthesize 3,6-dibromo-2,5-bis(tributylstannyl)thieno[3,2-*b*]thiophene (*cf.* ref. 1) we isolated along with this product (29% yield) the tetrasubstituted thiophene 7 (31%), both as colourless oils. In this case the alkyne-linked tributylstannyl group was lost during the work-up procedure.

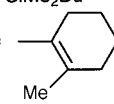
Trimethylsilyl groups are equally fragile. Thus, when 3,6-

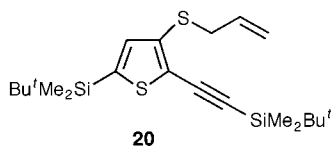
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- 5 $R^1 = R^3 = \text{SiMe}_2\text{Bu}^t$, $R^2 = \text{Bu}$
 6 $R^1 = R^3 = \text{Me}$, $R^2 = \text{Bu}$
 7 $R^1 = \text{SnBu}_3$, $R^2 = \text{Bu}$, $R^3 = \text{H}$
 8 $R^1 = R^3 = \text{H}$, $R^2 = \text{CH}_2\text{CH}=\text{CH}_2$
 9 $R^1 = \text{H}$, $R^2 = \text{Bu}$, $R^3 = 2\text{-thienyl}$
 10 $R^1 = R^3 = \text{SiMe}_2\text{Bu}^t$,
 $R^2 = \text{CH}_2\text{CH}=\text{CH}_2$



- 11 $R^1 = \text{Me}$, $R^2 = R^4 = \text{SiMe}_2\text{Bu}^t$, $R^3 = \text{Bu}$
 12 $R^1 = R^3 = \text{Bu}$, $R^2 = R^4 = \text{SiMe}_2\text{Bu}^t$
 13 $R^1 = R^3 = \text{Bu}$, $R^2 = R^4 =$ 
 14 $R^1 = R^3 = \text{Bu}$, $R^2 = R^4 = \text{H}$
 15 $R^1 = R^2 = R^3 = R^4 = \text{Me}$
 16 $R^1 = R^3 = \text{Me}$, $R^2 = R^4 = \text{SiMe}_2\text{Bu}^t$
 17 $R^1 = R^3 = \text{Me}$, $R^2 = \text{H}$, $R^4 = \text{SiMe}_2\text{Bu}^t$
 18 $R^1 = R^3 = \text{Li}$, $R^2 = R^4 = \text{SiMe}_2\text{Bu}^t$
 19 $R^1 = R^3 = \text{CH}_2\text{CH}=\text{CH}_2$, $R^2 = R^4 = \text{SiMe}_2\text{Bu}^t$



dibromo-2,5-bis(trimethylsilyl)thieno[3,2-*b*]thiophene¹ was treated with 2 mol equiv. of phenyllithium (THF, -78°C) and the resulting mixture was allowed to warm up to -30°C , then cooled down again to -78°C prior to addition of an excess of allyl bromide (3-bromopropene), the product isolated [by flash chromatography on an alumina column; light petroleum–ethyl acetate (10:1) as eluant] as a yellow oil was 3-allylsulfanyl-4-bromo-2-ethynylthiophene **8** (46% yield).

We attempted to synthesize 3,6-dibromo-2,5-bis(2-thienyl)thieno[3,2-*b*]thiophene by a Pd(0)-catalyzed [Pd(PPh₃)₄ in PhMe] coupling reaction between 2,3,5,6-tetrabromothieno[3,2-*b*]thiophene and 2 mol equiv. of 2-(tributylstannyl)thiophene¹⁶ but this gave only the monosubstituted product, 2,3,6-tribromo-5-(2-thienyl)thieno[3,2-*b*]thiophene (40% yield). When this was treated with 2 mol equiv. of butyllithium (THF, ambient temperature) initial Br→Li exchange occurred at positions-2 and -6 and a subsequent ring-opening reaction gave the 1,2-bis(2-thienyl)ethyne **9** (38% yield) as a yellow oil.

Next the product **5** of the ring-opening reaction of 3,6-dilithiated 2,5-bis(*tert*-butyldimethylsilyl)thieno[3,2-*b*]thiophene was treated successively with 1 mol equiv. of butyllithium (THF, 0°C) and an excess of iodomethane. Following the normal work-up procedure and flash chromatography of the crude product on silica [light petroleum–ethyl acetate (10:1) as eluant] this gave the enediyne **11** (89% yield) as a yellow oil. The advantage of the stepwise ring-opening procedure is that each of the thiolate anions generated can be captured by a different alkylating agent.

Both ring-opening processes can be carried out in tandem. Thus, when 2,3,5,6-tetrabromothieno[3,2-*b*]thiophene was converted *in situ* into 3,6-dibromo-2,5-bis(*tert*-butyldimethylsilyl)thieno[3,2-*b*]thiophene,¹ as described before, and a further 2 mol equiv. of butyllithium was added (THF, 0°C) prior to the reaction mixture being allowed to warm up to ambient temperature, it gave the enediyne **12** (70% yield) as a yellow oil. Enediyne **13** (36%) was prepared similarly from 3,6-dibromo-2,5-bis(2-methylcyclohex-1-enyl)thieno[3,2-*b*]thiophene.¹ In this reaction isomerisation of the double bond in the 2-methylcyclohex-1-enyl moiety also occurs during the reaction.

Removal of the TBDMS-protecting groups from enediyne **12** with tetrabutylammonium fluoride (THF, ambient temperature) gave the deprotected enediyne **14** (73.5%) which is extremely unstable.

A similar enediyne **15** was prepared in a different way. Thus, 2,3,5,6-tetrabromothieno[3,2-*b*]thiophene was treated successively with 4 mol equiv. of methylolithium and 2 mol equiv. of *tert*-butyldimethylsilyl chloride (THF, 0°C →ambient temperature). To the resulting mixture containing 3,6-dibromo-2,5-bis(*tert*-butyldimethylsilyl)thieno[3,2-*b*]thiophene was added a further 4 mol equiv. of methylolithium (THF, 0°C) followed by an excess of iodomethane (THF, 0°C →ambient temperature). Following the usual work-up procedure this gave enediyne **15** (62%) as a yellow oil.

Presumably the excess of methylolithium present throughout this procedure resulted in a loss of both TBDMS-protecting groups. When the amount of methylolithium used in each step was reduced from 4 to 2 mol equiv. a mixture of enediynes **16** (32% yield) and **17** (37%) was obtained (both are yellow oils).

Finally we attempted to alkylate each of the thiolate anionic centres in the ring-opened product **18**, derived from 3,6-dilithiated 2,5-bis(*tert*-butyldimethylsilyl)thieno[3,2-*b*]thiophene with allyl bromide. This gave a separable mixture of thiophenes **10** (17% yield) and **20** (27%), and the enediyne **19** (18% yield), all colourless oils. When this procedure was carried out again but with *sec*-butyllithium replacing the butyllithium, only the enediyne **19** (32%) was isolated.

Experimental

The instruments and general experimental procedures used were the same as described in Part 2¹ unless stated otherwise. Light petroleum refers to the fraction of bp range $40\text{--}60^\circ\text{C}$. Unless stated otherwise crude products were extracted from quenched (20% aqueous ammonium chloride used) reaction mixtures with ether and flash chromatographed on silica; light petroleum as eluant. The alkynes synthesized in this paper were unstable and satisfactory elemental analyses could not be carried out. Following suitable purification (one spot on TLC analysis) they were characterized by IR, ¹H NMR (in some cases ¹³C NMR in addition), and mass spectroscopy (low- and high-resolution).

2-(Tributylstannyl)thiophene,¹⁶ 2,3,5,6-tetrabromothieno[3,2-*b*]thiophene¹ and 2,5-dimethyl-, 2,5-bis(trimethylsilyl)- and 2,5-bis(6-methylcyclohex-1-enyl)-3,6-dibromothieno[3,2-*b*]thiophene¹ were prepared by literature procedures.

2,3,6-Tribromo-5-(2-thienyl)thieno[3,2-*b*]thiophene

2-(Tributylstannyl)thiophene (1.02 g, 2.7 mmol) was added to a stirred solution of 2,3,5,6-tetrabromothieno[3,2-*b*]thiophene (0.62 g, 1.36 mmol) and tetrakis(triphenylphosphine)palladium (0.19 g, 0.16 mmol) in anhydrous toluene (60 cm³) under nitrogen and the resulting mixture was heated under reflux for 20 h. The solvent was distilled off under reduced pressure and the crude product flash chromatographed on silica. Light petroleum eluted the *product* (0.25 g, 40%) as a yellow solid, mp 138–140 °C (from light petroleum–ethyl acetate); $\nu_{\max}/\text{cm}^{-1}$ 692 (C–Br); δ_{H} 7.11 (1 H, dd, $J_{4,5}$ 5.0, $J_{4,3}$ 4.0, H-4'), 7.41 (1 H, d, $J_{5,4}$ 5.0, H-5') and 7.45 (1 H, d, $J_{3,4}$ 4.0, H-3'); m/z 457 (8%), 459 (100%), 461 (99%), 463 (15%) (MH⁺) (Found: MH⁺, 456.7034. C₁₀H₃Br₃S₃ requires *MH*, 456.7072).

3-Bromo-2-*tert*-butyldimethylsilyl-5-*tert*-butyldimethylsilyl-ethynyl-4-butylsulfanylthiophene 5

Butyllithium (1.5 mol dm⁻³ in hexane; 0.72 cm³, 1.08 mmol) was added dropwise to a stirred solution of 2,3,5,6-tetrabromothieno[3,2-*b*]thiophene (0.244 g, 0.54 mmol) in tetrahydrofuran (50 cm³) at ambient temperature, the mixture was stirred for a further 10 min, then *tert*-butyldimethylsilyl chloride (0.2 g, 1.32 mmol) was added. The resulting mixture was cooled to -78 °C, a further quantity of butyllithium (1.5 mol dm⁻³ in hexane; 0.36 cm³, 0.54 mmol) was added, the solution was stirred at this temperature for a further 30 min, then it was allowed to warm up slowly to ambient temperature when it was quenched by addition of an excess of 20% ammonium chloride. Extraction with dichloromethane gave the crude product which was flash chromatographed on silica. Light petroleum eluted 3-bromo-2-*tert*-butyldimethylsilyl-5-*tert*-butyldimethylsilylethynyl-4-butylsulfanylthiophene **5** (0.19 g, 70%) as a yellow oil; $\nu_{\max}/\text{cm}^{-1}$ 2147 (C≡C); δ_{H} 0.17 (6 H, s, SiMe₂), 0.38 (6 H, s, SiMe₂), 0.86 (3 H, t, J 7.0, Me), 0.93 (9 H, s, SiBu-*tert*), 0.98 (9 H, s, SiBu-*tert*), 1.35–1.54 (4 H, m, 2 × CH₂) and 2.93 (2 H, t, J 7.0 Hz, SCH₂) (Found: MH⁺, 505.1270. C₂₂H₃₉-⁸¹BrSi₂S₂ requires *MH*, 505.1274).

3-Bromo-4-butylsulfanyl-2-methyl-5-(prop-1-ynyl)thiophene 6

Butyllithium (1.5 mol dm⁻³ in hexane; 0.3 cm³, 0.45 mmol) was added dropwise to a stirred solution of 3,6-dibromo-2,5-dimethylthieno[3,2-*b*]thiophene (68 mg, 0.21 mmol) in tetrahydrofuran (30 cm³) at ambient temperature, the resulting mixture was stirred for a further 3 h and then it was quenched. Work-up gave: (i) the *product* **6** (chromatographed twice on neutral alumina with light petroleum as eluant) (24 mg, 38%) as a colourless oil; δ_{H} 0.89 (3 H, t, J 7.0, Me), 1.19–1.60 (4 H, m, 2 × CH₂), 2.10 (3 H, s, 2-Me), 2.38 (2 H, s, C≡CMe) and 2.87 (2 H, t, J 7.0, SCH₂); m/z 335 (44%), 337 (100%) (MNH₄⁺) (Found: MH⁺, 302.9873. C₁₂H₁₅BrS₂ requires *MH*, 302.9877); and (ii) 2,5-dimethylthieno[3,2-*b*]thiophene (8 mg, 23%); δ_{H} 2.53 (6 H, d, J 0.7, 2 × Me) and 6.82 (2 H, d, J 0.7, H-3 and H-6); m/z 169 (MH⁺). A trace of 4,5-bis(butylsulfanyl)oct-4-ene-2,6-diyne (see later), arising from tandem ring-opening of the 3,6-dilithiated starting material, was detected by mass spectroscopy in the crude product; m/z 281 (MH⁺) but could not be isolated.

Synthesis of 3,6-dibromo-2,5-bis(tributylstannyl)thieno[3,2-*b*]thiophene; 3-bromo-2-tributylstannyl-4-butylsulfanyl-5-ethynylthiophene 7 as a by-product

Butyllithium (1.5 mol dm⁻³ in hexane; 0.80 cm³, 1.21 mmol) was added dropwise to a stirred solution of 2,3,5,6-tetrabromothieno[3,2-*b*]thiophene (0.25 g, 0.55 mmol) in tetrahydrofuran (50 cm³) at ambient temperature and the resulting mixture was stirred for a further 15 min. Then it was cooled down to -78 °C, tributylstannyl chloride (0.36 g, 1.10 mmol) was added, the mixture was stirred for a further 2 h at -78 °C,

then it was warmed up slowly to ambient temperature, and stirred overnight prior to quenching. Work-up in the usual way gave: (i) 3,6-dibromo-2,5-bis(tributylstannyl)thieno[3,2-*b*]thiophene as a colourless oil (0.12 g, 29%); δ_{H} 0.90 (18 H, t, 6 × Me), 1.21–1.56 (24 H, m, 12 × CH₂) and 1.59 (12 H, t, J 7.0, 6 × SnCH₂); m/z (FAB) 875 [Found (EI): M⁺ - 57 (Bu), 818.9280. C₃₀H₅₄Br₂S₂Sn₂ requires *M* - 57 (Bu), 818.9370]; and (ii) 3-bromo-2-tributylstannyl-4-butylsulfanyl-5-ethynylthiophene **7** (0.1 g, 31%) as a colourless oil; $\nu_{\max}/\text{cm}^{-1}$ 3311 (C≡C–H) and 2100 (C≡C); δ_{H} 0.83–1.59 [34 H, m, SnBu₃ + (CH₂)₂Me], 2.97 (2 H, t, J 7.5, SCH₂) and 3.62 (1 H, s, C≡CH); m/z 563, 565 (M⁺ + 1) (Found: MH⁺, 565.0602. C₂₂H₃₇BrS₂Sn requires *MH*, 565.0621).

3-Allylsulfanyl-4-bromo-2-ethynylthiophene 8

Phenyllithium (1.8 mol dm⁻³ in hexane; 0.19 cm³, 1.16 mmol) was added dropwise to a stirred solution of 3,6-dibromo-2,5-bis(trimethylsilyl)thieno[3,2-*b*]thiophene (0.08 g, 0.17 mmol) in tetrahydrofuran (50 cm³) at -78 °C, then the resulting mixture was allowed to warm up to -30 °C. It was cooled down again to -78 °C, allyl bromide (0.10 cm³, 0.14 g, 1.16 mmol) was added, the mixture was allowed to warm up slowly to ambient temperature at which point it was stirred for a further 1 h, then quenched and worked up. Light petroleum–ethyl acetate (10:1) eluted from the silica column 3-allylsulfanyl-4-bromo-2-ethynylthiophene **8** (0.02 g, 46%) as a yellow oil; $\nu_{\max}/\text{cm}^{-1}$ 3299 (C≡C–H) and 2287 (C≡C); δ_{H} 3.53 (2 H, d, J 7.0, SCH₂), 3.62 (1 H, s, C≡CH), 4.91 and 4.96 [2 H, 2 × dd (overlapping), CH=CH₂], 5.80 (1 H, tdd, CH=CH₂) and 7.23 (1 H, s, H-5) (Found: MH⁺, 258.9238. C₉H₇BrS₂ requires *MH*, 258.9251).

1-(2-Thienyl)-2-(4-bromo-3-butylsulfanyl-2-thienyl)ethyne 9

Butyllithium (1.5 mol dm⁻³ in hexane; 0.8 cm³, 1.2 mmol) was added dropwise to a stirred solution of 2,3,6-tribromo-5-(2-thienyl)thieno[3,2-*b*]thiophene (0.25 g, 0.54 mmol) in tetrahydrofuran (30 cm³) at ambient temperature and the resulting mixture was stirred for a further 12 h, then quenched. Work-up in the usual way gave the *product* **9** (72 mg, 38%) as a yellow oil; $\nu_{\max}/\text{cm}^{-1}$ 2195 (C≡C); δ_{H} 0.87 (3 H, t, J 7.0, Me), 1.21–1.67 (4 H, m, 2 × CH₂), 2.95 (2 H, t, 7.0, SCH₂), 7.02 (1 H, dd, $J_{4,5}$ 5.0, $J_{4,3}$ 4.0, H-4'), 7.25 (1 H, s, H-5), 7.30 (1 H, dd, $J_{3,4}$ 4.0, $J_{3,5}$ 1.0, H-3') and 7.33 (1 H, dd, $J_{5,4}$ 5.0, $J_{5,3}$ 1.0, H-5'); m/z 357, 359 (MH⁺) (Found: MH⁺, 356.9436. C₁₄H₁₃BrS₃ requires *MH*, 356.9442).

(*E*)-1,6-Bis(*tert*-butyldimethylsilyl)-3-butylsulfanyl-4-methylsulfanylhex-3-ene-1,5-diyne 11

Butyllithium (1.37 mol dm⁻³ in hexane; 0.1 cm³, 0.14 mmol) was added to a stirred solution of 3-bromo-2-*tert*-butyldimethylsilyl-5-*tert*-butyldimethylsilylethynyl-4-butylsulfanylthiophene **5** (0.06 g, 0.12 mmol) in tetrahydrofuran (50 cm³) at 0 °C followed by iodomethane (0.1 cm³, 0.23 g, 1.6 mmol, an excess) and the resulting mixture was stirred for 1 h before being quenched. Work-up in the usual way [light petroleum–ethyl acetate (10:1) as eluant] gave (*E*)-1,6-bis(*tert*-butyldimethylsilyl)-3-butylsulfanyl-4-methylsulfanylhex-3-ene-1,5-diyne **11** (0.045 g, 89%) as a yellow oil; $\nu_{\max}/\text{cm}^{-1}$ 2137 (C≡C); δ_{H} 0.15 (12 H, s, 2 × SiMe₂), 0.89 (3 H, t, J 7.0, Me), 0.96 (18 H, s, 2 × SiBu-*tert*), 1.30–1.65 (4 H, m, 2 × CH₂), 2.41 (3 H, s, SMe) and 2.88 (2 H, t, J 7.0, SCH₂) (Found: MH⁺, 439.2331. C₂₃H₄₂Si₂S₂ requires *MH*, 439.2345).

(*E*)-1,6-Bis(*tert*-butyldimethylsilyl)-3,4-bis(butylsulfanyl)hex-3-ene-1,5-diyne 12

Butyllithium (1.37 mol dm⁻³ in hexane; 1.6 cm³, 2.20 mmol) was added dropwise to a solution of 2,3,5,6-tetrabromothieno[3,2-*b*]thiophene (0.5 g, 1.11 mmol) in tetrahydrofuran (100 cm³) at ambient temperature followed by *tert*-butyl-

dimethylsilyl chloride (0.33 g, 2.20 mmol) and the resulting mixture was stirred until (~30 min) TLC analysis indicated the presence of one major product. The mixture was cooled to 0 °C, a further portion of butyllithium (1.37 mol dm⁻³ in hexane; 1.6 cm³, 2.20 mmol) was added, the mixture was stirred overnight, then it was quenched. Extraction with dichloromethane gave the crude product which was flash chromatographed on silica. Light petroleum eluted (*E*)-1,6-bis(*tert*-butyldimethylsilyl)-3,4-bis(*butylsulfanyl*)hex-3-ene-1,5-diyne **12** (0.375 g, 70%) as a yellow oil; $\nu_{\max}/\text{cm}^{-1}$ 2137 (C≡C); δ_{H} 0.15 (12 H, s, 2 × SiMe₂), 0.89 (6 H, t, *J* 7.0, 2 × Me), 0.96 (18 H, s, 2 × SiBu-*tert*), 1.32–1.68 (8 H, m, 4 × CH₂) and 2.89 (4 H, t, *J* 7.0, 2 × SCH₂); δ_{C} -4.68, 13.66, 16.72, 21.87, 26.11, 32.43, 33.06, 98.98, 109.62, 122.94 (Found: MH⁺, 481.2812. C₂₆H₄₈Si₂S₂ requires *MH*, 481.2814).

(*E*)-1,6-Bis(2-methylcyclohex-1-enyl)-3,4-bis(*butylsulfanyl*)hex-3-ene-1,5-diyne **13**

Butyllithium (1.37 mol dm⁻³ in hexane; 1.1 cm³, 1.51 mmol) was added to a stirred solution of 3,6-dibromo-2,5-bis(6-methylcyclohex-1-enyl)thieno[3,2-*b*]thiophene (0.24 g, 0.49 mmol) in tetrahydrofuran (50 cm³) at ambient temperature; the resulting mixture was stirred for a further 2 h, then it was quenched. Work-up (the crude product was chromatographed twice) gave 1,6-bis(2-methylcyclohex-1-enyl)-3,4-bis(*butylsulfanyl*)hex-3-ene-1,5-diyne **13** (0.08 g, 36%) as a colourless oil; $\nu_{\max}/\text{cm}^{-1}$ 2190 (C≡C); δ_{H} 0.88 (6 H, t, *J* 7.0, 2 × Me), 1.08–2.37 (16 H, m, 8 × CH₂), 1.55 (6 H, s, 2 × C=CMe) and 2.90 (4 H, t, *J* 7.0, 2 × SCH₂) (Found: MH⁺, 441.2643. C₂₈H₄₀S₂ requires *MH*, 441.2649).

3,4-Bis(*butylsulfanyl*)hex-3-ene-1,5-diyne **14**

Tetrabutylammonium fluoride (1.0 mol dm⁻³ in tetrahydrofuran; 0.69 cm³, 0.69 mmol) was added to a stirred solution of 1,6-bis(*tert*-butyldimethylsilyl)-3,4-bis(*butylsulfanyl*)hex-3-ene-1,5-diyne **12** (0.13 g, 0.27 mmol) in tetrahydrofuran (50 cm³), the resulting mixture was stirred for a further 15 min, then quenched by addition of an excess (50 cm³) of water. Extraction with ether gave the crude product which was flash chromatographed on silica. Light petroleum eluted 3,4-bis(*butylsulfanyl*)hex-3-ene-1,5-diyne **14** (0.05 g, 73.5%) which began to decompose immediately it was isolated; $\nu_{\max}/\text{cm}^{-1}$ 3280 (C≡C–H) and 2091 (C≡C); δ_{H} 0.89 (6 H, t, *J* 7.0, 2 × Me), 1.39–1.62 (8 H, m, 4 × CH₂), 2.92 (4 H, t, *J* 7.0, 2 × SCH₂) and 3.95 (2 H, s, 2 × C≡CH) (Found: MNH₄⁺, 270.1349. C₁₄H₂₀S₂ requires *MNH*₄, 270.1350).

4,5-Bis(*methylsulfanyl*)oct-4-ene-2,6-diyne **15**

Methylithium (1.6 mol dm⁻³ in hexane; 1.31 cm³, 2.10 mol) was added dropwise to a stirred solution of 2,3,5,6-tetrabromothieno[3,2-*b*]thiophene (0.22 g, 0.48 mmol) in tetrahydrofuran (50 cm³) at 0 °C, the resulting mixture was stirred for a further 15 min, then *tert*-butyldimethylsilyl chloride (0.15 g, 0.99 mmol) was added. A further quantity of methylithium (1.6 mol dm⁻³ in hexane; 1.31 cm³, 2.10 mmol) was added at 0 °C followed by iodomethane (0.12 cm³, 0.27 g, 1.92 mmol), then the mixture was allowed to warm to ambient temperature at which point it was stirred for a further 2 h prior to being quenched. Work-up gave 4,5-bis(*methylsulfanyl*)oct-4-ene-2,6-diyne **15** (0.058 g, 62%) as a yellow oil; $\nu_{\max}/\text{cm}^{-1}$ 2138 (C≡C); δ_{H} 2.05 (6 H, s, 2 × C≡CMe) and 2.42 (6 H, s, 2 × SMe) [Found (EI): MH⁺, 197.0466. C₁₀H₁₂S₂ requires *MH*, 197.0459].

1,6-Bis(*tert*-butyldimethylsilyl)-3,4-bis(*methylsulfanyl*)hex-3-ene-1,5-diyne **16**

Methylithium (1.6 mol dm⁻³ in hexane; 0.61 cm³, 0.98 mmol) was added dropwise to a stirred solution of 2,3,5,6-tetrabromothieno[3,2-*b*]thiophene (0.22 g, 0.49 mmol) in tetrahydrofuran (50 cm³) at 0 °C, the resulting mixture was stirred at

ambient temperature for 15 min, then *tert*-butyldimethylsilyl chloride (0.15 g, 0.99 mmol) was added at 0 °C. A further quantity of methylithium (1.6 mol dm⁻³ in hexane; 0.61 cm³, 0.98 mmol) was added at 0 °C followed by iodomethane (0.12 cm³, 0.27 g, 1.92 mmol), the resulting mixture was stirred for a further 2 h at ambient temperature, then it was quenched. Work-up gave: (i) 1,6-bis(*tert*-butyldimethylsilyl)-3,4-bis(*methylsulfanyl*)hex-3-ene-1,5-diyne **16** (0.06 g, 32%) as a yellow oil; $\nu_{\max}/\text{cm}^{-1}$ 2137 (C≡C); δ_{H} 0.16 (12 H, s, 2 × SiMe₂), 0.96 (18 H, s, 2 × SiBu-*tert*) and 2.41 (6 H, s, 2 × SMe) (Found: MH⁺, 397.1859. C₂₀H₃₆Si₂S₂ requires *MH*, 397.1875); and (ii) 1-*tert*-butyldimethylsilyl-3,4-bis(*methylsulfanyl*)hex-3-ene-1,5-diyne **17** (0.05 g, 37%) as a yellow oil; $\nu_{\max}/\text{cm}^{-1}$ 2138 (C≡C); δ_{H} 0.16 (6 H, s, 2 × SiMe₂), 0.98 (9 H, s, SiBu-*tert*), 2.40 (1 H, s, C≡CH), 2.41 (3 H, s, SMe) and 2.48 (3 H, s, SMe) (Found: MH⁺, 283.1005. C₁₄H₂₂Si₂S₂ requires *MH*, 283.1010).

Treatment of 3,6-dibromo-2,5-bis(*tert*-butyldimethylsilyl)-thieno[3,2-*b*]thiophene with organolithium reagents followed by an allyl bromide quench

(a) **With butyllithium.** Butyllithium (1.37 mol dm⁻³ in hexane; 0.3 cm³, 0.41 mmol) was added dropwise to a solution of 2,3,5,6-tetrabromothieno[3,2-*b*]thiophene (0.17 g, 0.37 mmol) in tetrahydrofuran (50 cm³) at ambient temperature, the resulting mixture was stirred for a further 5 min, then *tert*-butyldimethylsilyl chloride (0.07 g, 0.46 mmol) was added and the mixture was stirred at ambient temperature for 15 min more. Then it was cooled down to -78 °C, a further quantity of butyllithium (1.37 mol dm⁻³ in hexane; 0.3 cm³, 0.41 mmol) was added followed by more *tert*-butyldimethylsilyl chloride (0.07 g, 0.46 mmol), then the resulting mixture was stirred at -78 °C for a further 30 min. More butyllithium (1.37 mol dm⁻³ in hexane; 0.6 cm³, 0.82 mmol) was added followed by allyl bromide (0.2 cm³, 0.28 g, 2.31 mmol) and the mixture was allowed to warm up slowly to ambient temperature when it was stirred for a further 1 h before being quenched. Work-up gave: (i) 4-allylsulfanyl-3-bromo-2-*tert*-butyldimethylsilyl-5-(*tert*-butyldimethylsilylethynyl)thiophene **10** (0.03 g, 17%) as a colourless oil; $\nu_{\max}/\text{cm}^{-1}$ 2147 (C≡C); δ_{H} 0.18 (6 H, s, SiMe₂), 0.38 (6 H, s, SiMe₂), 0.92 (9 H, s, SiBu-*tert*), 0.99 (9 H, s, SiBu-*tert*), 3.53 (2 H, d, *J* 7.0, SCH₂), 4.91 (1 H, d, *J* 11.0, CH=CH₂), 4.95 (1 H, d, *J* 17.0, CH=CH₂) and 5.67–5.84 (1 H, m, CH=CH₂) (Found: MNH₄⁺, 504.1242. C₂₁H₃₅BrSi₂S₂ requires *MNH*₄, 504.1246); (ii) 3-allylsulfanyl-5-*tert*-butyldimethylsilyl-2-(*tert*-butyldimethylsilylethynyl)thiophene **20** (0.04 g, 27%) as a colourless oil; $\nu_{\max}/\text{cm}^{-1}$ 2142 (C≡C); δ_{H} 0.17 (6 H, s, SiMe₂), 0.23 (6 H, s, SiMe₂), 0.88 (9 H, s, SiBu-*tert*), 0.99 (9 H, s, SiBu-*tert*), 3.56 (2 H, d, *J* 7.0, SCH₂), 4.90 (1 H, d, *J* 11.0, CH=CH₂), 5.01 (1 H, d, *J* 17.0, CH=CH₂) and 5.75–5.92 (1 H, m, CH=CH₂) (Found: MH⁺, 409.1862. C₂₁H₃₅Si₂S₂ requires *MH*, 409.1875); and (iii) 3,4-bis(*allylsulfanyl*)-1,6-bis(*tert*-butyldimethylsilyl)hex-3-ene-1,5-diyne **19** (0.03 g, 18%) as a colourless oil; $\nu_{\max}/\text{cm}^{-1}$ 2138 (C≡C); δ_{H} 0.15 (12 H, s, 2 × SiMe₂), 0.96 (18 H, s, 2 × SiBu-*tert*), 3.56 (4 H, d, *J* 7.0, 2 × SCH₂), 5.06 (1 H, dd, *J* 10.0, *J* 1.0, CH=CH₂), 5.18 (1 H, dd, *J* 17.0, *J* 1.0, CH=CH₂) and 5.78–5.93 (1 H, m, CH=CH₂); δ_{C} -4.68, 16.73, 26.13, 36.28, 99.04, 110.45, 117.55, 122.98 and 133.93 (Found: MH⁺, 449.2189. C₂₄H₄₀Si₂S₂ requires *MH*, 449.2188).

(b) **With *sec*-butyllithium.** *sec*-Butyllithium (1.1 mol dm⁻³ in hexane; 1.33 cm³, 1.46 mmol) was added dropwise to a stirred solution of 2,3,5,6-tetrabromothieno[3,2-*b*]thiophene (0.33 g, 0.73 mmol) in tetrahydrofuran (50 cm³) at ambient temperature, the mixture was stirred for a further 15 min, then *tert*-butyldimethylsilyl chloride (0.22 g, 1.46 mmol) was added and the resulting mixture was stirred for a further 1 h. A further amount of *sec*-butyllithium (1.1 mol dm⁻³ in hexane; 1.33 cm³, 1.46 mmol) was added followed, after 10 min, by addition of allyl bromide (0.18 g, 0.12 cm³, 1.48 mmol) and the mixture was

stirred at ambient temperature overnight. Work-up as described in (a) afforded 3,4-bis(allylsulfanyl)-1,6-bis(*tert*-butyldimethylsilyl)hex-3-ene-1,5-diyne **19** (0.105 g, 32%) as a colourless oil, identical (IR, ¹H NMR and mass spectroscopy) with the sample prepared as described in (a).

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